Title: **Analysis of Bromine-Mercury Reactions in Flue Gas**

Authors: Geoffrey D. Silcox (PI), JoAnn S. Lighty (co-PI)
Student: Brydger Cauch
Institution University of Utah
Department of Chemical Engineering
50 S. Central Campus Drive, RM 3290 MEB
Salt Lake City, Utah 84112
Phone: (801)581-8820, (801)581-5763
Fax: (801)585-9291
Email: geoff@che.utah.edu, jlighty@coe.utah.edu
Subcontractor Constance L. Senior
Reaction Engineering International

Grant Number DE-FG26-06NT42713
Period of Performance: January 2006 – January 2009
Date April 4, 2006

Objectives

At flame temperatures, mercury exists entirely in its elemental form (Hg^o). In the absence of halogens, mercury tends to remain in the elemental form as the combustion gases cool. The elemental form is difficult to remove from exhaust gases. Oxidized forms of mercury, such as $HgCl_2$ and $HgBr_2$, are easily removed using existing air pollution control equipment. They are also readily adsorbed by carbon-based sorbents. There is considerable experimental and theoretical evidence that the oxidation of mercury in combustion systems can be achieved by the direct injection of bromine-containing compounds. The data show that bromine is much more effective than chlorine at oxidizing Hg^o. The objectives of this project are (1) to understand the fundamental chemistry of bromine and mercury that leads to the oxidized form of mercury, $HgBr_2$, and (2) to be able to predict the extent of oxidation for industrial applications.

Accomplishments to Date

We have completed a review of the literature on mechanisms and models for bromine-mercury reactions. This has included equilibrium thermodynamics, bromine chemistry in combustion systems, bromine-mercury reactions, atmospheric chemistry of mercury and bromine, and full-scale test results on bromine injection. The full-scale data show that Br is highly effective at oxidizing Hg. Brominated activated carbon is effective at capturing Hg, even in hot-side ESP applications. Thermodynamic calculations and preliminary kinetic calculations show that HBr is unstable, relative to HCl, and that significant concentrations of Br and Br_2 are available to react with mercury at temperatures below 900K.

The atmospheric chemistry literature supports the following mechanism for oxidation of mercury by bromine.

$$Br_2 + h\nu \rightarrow 2Br$$
$$Hg + Br \rightarrow HgBr$$
$$HgBr + Br \rightarrow HgBr_2$$
$$HgBr + Br_2 \rightarrow HgBr_2 + Br$$

This mechanism is analogous to the accepted pathway for Cl and Hg. Rate constants for the above reactions are available in the atmospheric chemistry literature but in many cases only at temperatures less than 300 K.

Future Work

The project will investigate bromine-mercury chemistry in experiments conducted in a bench-scale, natural gas-fired, flow reactor. An improved understanding of the fundamental chemistry will allow optimization of the bromine injection process to enhance the formation of $HgBr_2$. Key parameters that will be considered include the temperature profile in the reaction zone, and the concentrations of NO_x, SO_2, moisture, and surface to volume ratio (m^2/m^3) in the reactor. The latter will include fixed bed studies of the effect of coal fly ash. A model of the oxidation process will be developed. We will use CHEMKIN 4.0 to examine practical application of various injection schemes under a variety of boiler conditions.

List of Conference Presentations

Mechanisms and Models for Hg Oxidation Reactions. G. Silcox, A. Fry, J. Lighty, C. Senior. Mercury, Trace Metals, and Fine Particulates – Issues and Solutions, Topic-Oriented Technical Meeting 28, American Flame Research Committee/International Flame Research Foundation. University of Utah. March 13-14, 2006.

Students Supported Under this Grant

Brydger Cauch, M.S. Candidate, U of Utah. Estimated starting date, June 2006.